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**Probing the dynamics of crystal nucleation via measurements  
of emission lifetimes in crystalloluminescence of sodium chloride**

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**Abstract**

We report measurements of the time dependence of photoemission events in crystalloluminescence (XTL) of sodium chloride. Aqueous solutions of NaCl were intentionally doped with trace amounts of copper and silver ions, and crystallization was induced by mixing with HCl. The mean lifetime for solutions doped only with copper ions was  $39.9 \pm 0.8 \mu\text{s}$ , which is close to the ultraviolet photoluminescence lifetime of solid NaCl doped with  $\text{Cu}^+$ . The rise time for emission events indicates that crystal nuclei are formed within 10 ns. A possible mechanism for reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  during nucleation is discussed. The mean lifetime for solutions doped with a mixture of silver and copper ions was  $12.7 \pm 0.7 \mu\text{s}$ , which suggests that electronic energy transfer takes place between  $\text{Ag}^+$  and dimer  $(\text{Ag}^+)_2$  species in the crystal lattice. Co-incident radiofrequency and acoustic signals were not detected, indicating that triboluminescence by crystal fracture is not a significant mechanism for XTL. The results demonstrate that dopant metal ions act as valuable indicators of the electronic environment during transformation of a solute cluster to a crystal nucleus.

**Keywords:** A1. Nucleation; A1. Doping; B1. Sodium chloride; B2. Phosphors

**1. Introduction**

Crystalloluminescence (XTL) is the emission of light during crystallization;<sup>1</sup> the first published reports of the phenomenon date back to the late 18<sup>th</sup> century. XTL has been observed in a variety of systems, including both melt and solution, and for both organic and inorganic compounds. There is no single mechanism to describe XTL.<sup>2</sup> In some systems, the emission can be traced to chemical reactions that occur during the crystallization, i.e., chemiluminescence (CL). In other systems, the emission results from fracture of nascent crystals, resulting in so-called

triboluminescence (TL). Although the phenomenon has not been studied widely, XTL has important applications in understanding mechanisms of nucleation and crystal growth.<sup>3-4</sup>

The XTL of sodium chloride was first described by Ernst Bandrowski in 1894.<sup>5</sup> It can be observed by rapidly precipitating NaCl from solution by adding ethanol or concentrated hydrochloric acid. The XTL appears as flashes of light throughout the solution, which develop over a period of minutes. Weiser was the first to make a systematic study of the effects of various physical and chemical parameters: including temperature, solution concentrations, and velocity of mixing.<sup>6</sup> He found that the intensity of emission did not increase with rate of precipitation, as would be expected for CL. Likewise, the intensity did not increase with agitation of the precipitate, from which he argued that TL was not the underlying cause. Through careful purification and doping procedures, Garten and Head demonstrated that trace amounts of metal-ion impurities were necessary to observe XTL of NaCl.<sup>7</sup> They also found that the number of photons detected was roughly proportional to the number of crystals obtained. They proposed that the metal ions are excited when a liquid-like solute cluster “clicks”, i.e., forms rapidly, into crystalline form.<sup>8-9</sup> They estimated that local supersaturations of the order of  $S = 14$  are required to cause primary homogeneous nucleation. This explains the requirements for concentrated reactant solutions and rapid mixing. The picture of nucleation, which proceeds first by localized increase of density, and then by change in structure to become crystalline, is what we now call two-step nucleation.<sup>3-4, 10-15</sup> The two-step model is in contrast to the classical nucleation theory based on the sequential addition of solute units to build a critical nucleus that is inherently crystalline.

The color of light from XTL of NaCl has been variously described as violet, bluish-green, blue or white.<sup>5, 16-18</sup> Early attempts to measure the emission spectrum produced conflicting results due to the low intensities of light and limited wavelength range of available photodetectors.<sup>18-19</sup> Barsanti and Maccaronne showed that XTL of NaCl solutions doped with copper ions gave an emission peak at 350 nm.<sup>1</sup> More recently our group have obtained fully dispersed spectra of XTL in the region 200–650 nm in NaCl solutions doped with trace amounts of copper and silver ions. Bands in the ultraviolet (UV) were attributed to  $d^9s^1 \rightarrow d^{10}$  emissions from the lowest triplet ( $^3E_g$ ) states of  $Ag^+$  (250 nm) and  $Cu^+$  (350 nm) ions. These ions substitute for  $Na^+$  cations in the NaCl lattice. A band in the visible region (425 nm) was assigned to emission from  $(Ag^+)_2$  pair centers.<sup>20</sup> The variety of colors for XTL of NaCl described by previous observers is likely to be due in part to differences in the impurities that happened to be present in the starting materials.

The time-dependence of sodium chloride XTL emissions at short times was first measured by Garten and Head.<sup>7</sup> They found that XTL of NaCl solutions doped with lead ions consisted of sequences of discrete pulses of light, each pulse having duration of ~80 ns. By contrast, in solutions doped with copper ions, each emission consisted of a train of photons with decaying intensity lasting hundreds of microseconds; emission lifetimes were not measured. The difference in behavior between copper (Group 11) and lead (Group 14) metal ions was attributed to the emitting metal-ion species occupying different locations within the nucleating clusters.<sup>8</sup> With silver ions as dopant, Garten and Head found that the solid NaCl recovered from solution was in the form of aggregates of small crystals. It was suggested that nucleation may be triggered as a chain-reaction in a group of adjacent clusters.<sup>7</sup> They estimated the size of the smallest nucleus to be circa 3.4 nm (approximately 2600 ion pairs) but the assumptions employed were primitive.

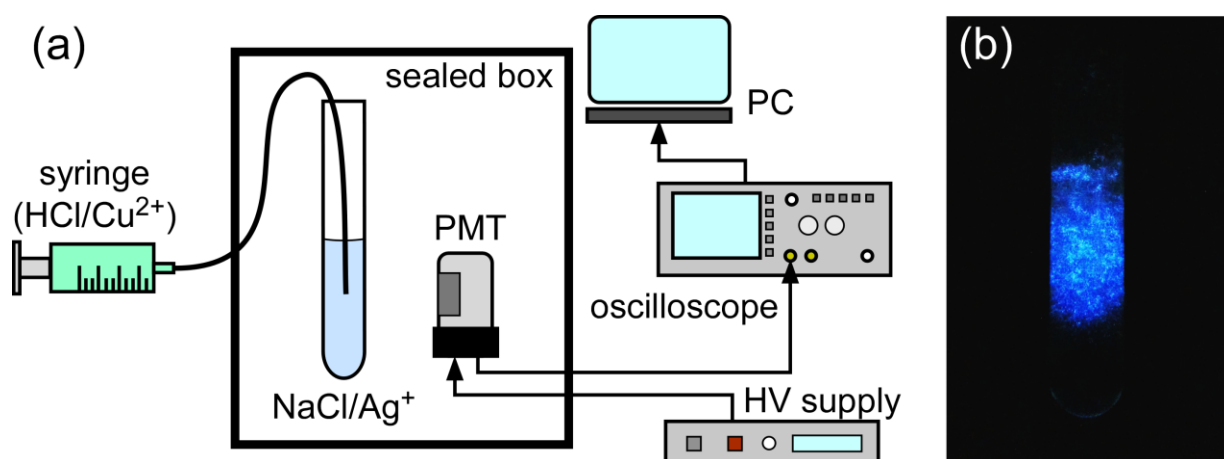
At the present time it is not clear if the XTL of substituent metal species in NaCl is due to electronic excitation from rapid transformation of solute cluster to crystal, or due to optical excitation by TL. When crystals of an inorganic salt are crushed in the presence of air, the emissions typically consist of narrow vibronic bands from  $N_2$  and  $N_2^+$  in the region 300–400 nm, commonly referred to as triboluminescence.<sup>21</sup> These emissions result from electrical discharges between newly formed charged surfaces. Under vacuum, the TL of solid NaCl shows a broad emission (400–700 nm) with a maximum at 460 nm. This broad emission has been considered to be due to luminescence from cation vacancies, excited by frictional abrasion.<sup>22</sup> For XTL of NaCl in solution, it is possible that the fracturing of newly formed crystals excites the luminescence of dopant metal-ions, i.e., optical emission due to TL.

In order to understand the mechanism for excitation and luminescence of metal-ion dopants in XTL of NaCl, we have quantified the emission lifetimes. To determine if there are weak emission bands due to TL, we have attempted to detect radio-frequency (RF) and acoustic emissions. These type of emissions have been detected during XTL in systems where the mechanism of crystal fracture is known to cause TL, for example, in  $Ba(ClO_3)_2$  and  $K_3Na(SO_4)_2$ .<sup>23</sup>

## 2. Experimental methods

The basic recipe used for inducing XTL by mixing solutions of HCl with NaCl has been described previously.<sup>24</sup> All solutions were prepared using deionized water (Fisher, HPLC grade, 2 M $\Omega$  cm). We report concentrations in terms of molality (moles of solute per kg of solvent). A stock solution of HCl (6.6 mol kg<sup>-1</sup>, 19% w/w) was prepared using concentrated HCl (36% w/w, Fisher

Scientific, AR Grade). A nearly saturated ( $6.0 \text{ mol kg}^{-1}$ ; supersaturation,  $S = 97\%$ ) stock solution of salt was prepared from solid NaCl (Sigma-Aldrich, Reagent-Plus 99.5+%). The dopants and concentrations were chosen to allow direct comparison with our previously reported emission spectra.<sup>24</sup> When both copper and silver are doped into the crystallizing solution, strong XTL can be obtained. As we have noted previously, doping only with silver ions produces relatively weak luminescence, and the reasons for this are not known. Solid  $\text{CuSO}_4$  (Fisher, Analysis Grade, 99.5+%) and  $\text{AgNO}_3$  (Fisher, Reagent Grade, 99.8+%) were used to prepare aqueous solutions for doping. A schematic of the experimental setup is shown in Figure 1. Experiments were conducted at the ambient temperature of  $20^\circ\text{C}$ . Approximately 5 mL of NaCl solution was doped with 0.0–0.2 mL of  $0.071 \text{ mol kg}^{-1}$   $\text{AgNO}_3$  solution in a fused-silica test-tube (16 mm diameter  $\times$  150 mm length). A syringe was filled with 5 mL of HCl solution doped with 0.05 mL of  $1.01 \text{ mol kg}^{-1}$   $\text{CuSO}_4$  solution. The test-tube was placed 60 mm from a photomultiplier tube (PMT, Hamamatsu R928, operated at  $-1 \text{ kV}$ ) in a sealed box to minimize interference from ambient light. No optical filters were used; emissions in the range 200–600 nm were detected. We note that the quantum efficiency ( $q$ ) of the PMT does not vary significantly over the range of expected emission wavelengths:  $\text{Ag}^+$  (25% at 250 nm),  $\text{Cu}^+$  (24% at 350 nm) and  $(\text{Ag}^+)_2$  (21% at 425 nm).

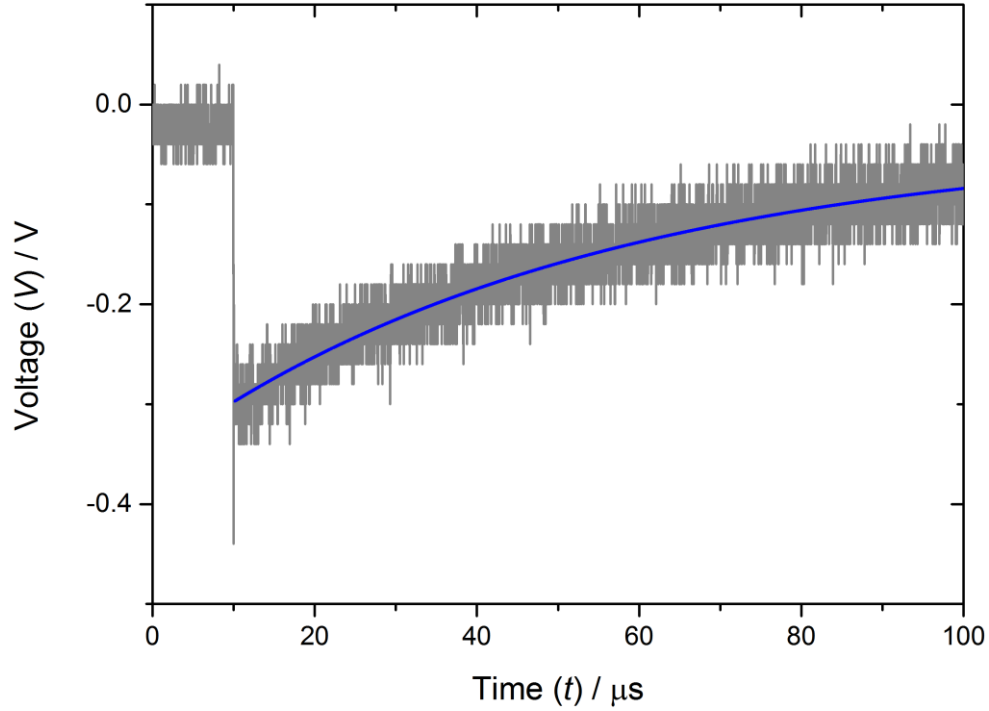


**Figure 1.** (a) Schematic diagram of experimental setup. Concentrated HCl solution (doped with copper ions) is mixed with nearly saturated NaCl solution (doped with silver ions) in a fused-silica test-tube. The time-dependent flashes of light from the resulting XTL were measured using a photomultiplier tube (PMT) coupled to an oscilloscope. (b) Photograph illustrating XTL in a test tube (exposure time 0.5 s. Note that the contrast of this image has been enhanced). The XTL is most intense in the region where the solutions mix rapidly.

Nucleation was forced by rapidly adding the HCl solution by syringe into the NaCl solution. Signals from the PMT were recorded using a digital storage oscilloscope (Tektronix TDS 3012B) and downloaded for offline analysis. A voltage threshold was used to trigger the oscilloscope to capture individual XTL events. For comparison to previous works, parts-per-million (ppm) mole ratios of dopant metal-ion relative to  $\text{Na}^+$  in the final mixed solution were calculated. All HCl solutions were doped to give 1900 ppm  $\text{Cu}^{2+}/\text{Na}^+$ . In addition to the copper doping, NaCl solutions were doped to give either 0 ppm  $\text{Ag}^+/\text{Na}^+$  (i.e., copper only) or 530 ppm  $\text{Ag}^+/\text{Na}^+$  (i.e., both silver and copper ions in solution). By comparison, we estimate the total impurity ion content from the de-ionized water to be 1 ppm relative to  $\text{Na}^+$ . It should be noted that these ratios are only a guide to the relative concentrations of dopants available in solution. The concentration of dopants in each nucleus is expected to vary considerably due to fluctuations in local supersaturation.

In order to determine if there were RF emissions due to TL, a simple antenna was assembled following the method of Garcia-Fernandez.<sup>25</sup> This consisted of a copper wire (1 m length) bent into a planar spiral shape, suspended above a petri dish containing the NaCl solution. As described above, both solutions were doped with metal ions, and crystallization was initiated by injecting the HCl solution by syringe. The antenna was connected to the oscilloscope, and the setup was tested by observing signals from small electrical discharges nearby using a piezoelectric anti-static gun (Milty Zerostat 3). The sensitivity of the setup was estimated to be  $-47$  dBm at 40 MHz ( $50\ \Omega$  impedance).

To detect if there were acoustic emissions during XTL, a custom-built hydrophone was used. A piezoelectric disc (12 mm diameter, Murata 7BB-12-9) was sealed between two glass coverslips using optical adhesive (Norland NOA 61). The signal was collected through a broadband preamplifier circuit and recorded using an oscilloscope. The disc assembly was submerged in the test-tube containing NaCl, and HCl was added by syringe, as described above. The sound produced during mixing provided an internal test for the functionality of the hydrophone.



**Figure 2.** Example of a decay event observed for XTL of NaCl solution doped with copper ions (copper only). The grey line is the experimental data, the blue line represents an exponential model function (here  $\tau = 52.7 \mu\text{s}$ ) obtained by a nonlinear least-squares fit to the experimental data.

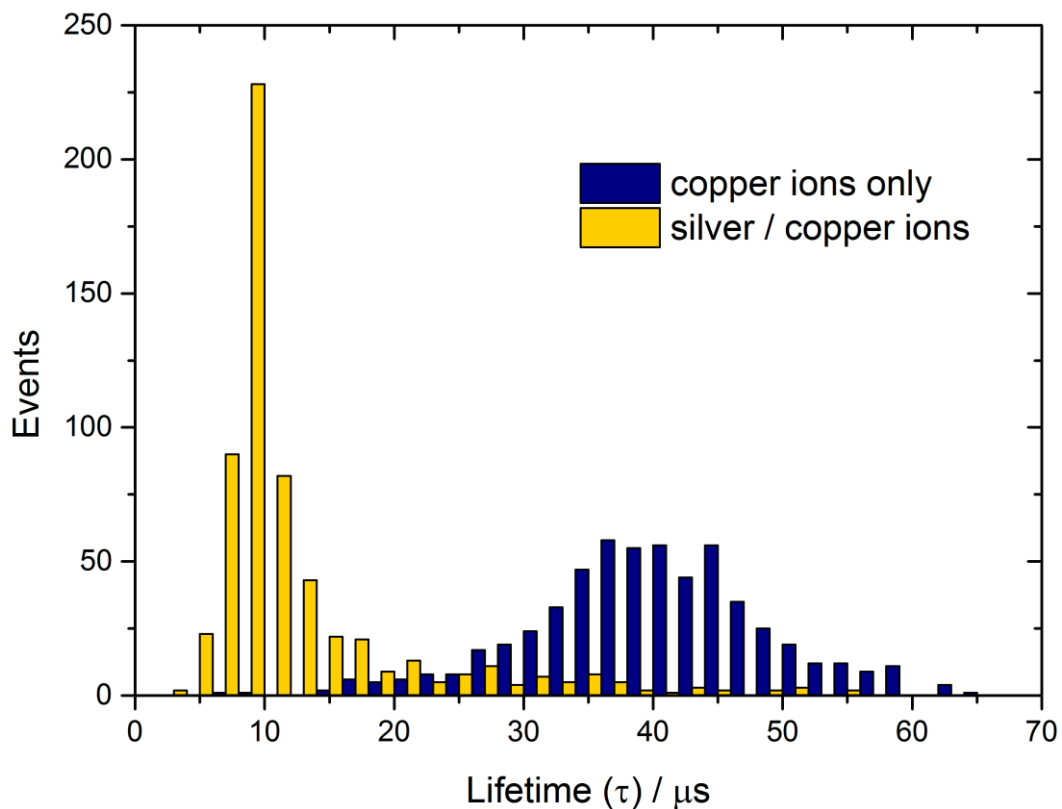
### 3. Results

Despite various attempts, no RF or acoustic emissions were detected during XTL of NaCl. The absence of such emissions show that the dominant mechanism in this system is not due to TL.<sup>6-7</sup> An example photoemission event, measured with the PMT, is shown in Figure 2. The time resolution of the oscilloscope was 10 ns per data point. The transit-time spread of electrons in the PMT, according to the manufacturer, was 1.2 ns. It can be seen that the signal rises sharply, which suggests that nucleation takes place within 10 ns. This is commensurate with the time for nucleation ( $< 5 \text{ ns}$ ) estimated by Garten and Head for NaCl doped with  $\text{Pb}^{2+}$ .<sup>8</sup> A total of 1784 events were recorded for solutions doped with copper ions only; 1551 events were recorded for solutions doped with both silver and copper ions. Many events recorded included stray (background) photons or overlapping emission events. Such events were excluded from further analysis. The remaining emission events were each fitted in turn (by a nonlinear least-squares method) using a single exponential function,  $V(t) = A \exp(-t/\tau) + V_0$ ; where  $V$  is the signal voltage,  $V_0$  is an offset voltage,  $A$  is the amplitude,  $t$  is time and  $\tau$  is the  $1/e$  decay lifetime. Including two or more

exponential decay times did not significantly improve the fits. Histograms of the lifetimes are plotted in Figure 3, and the mean lifetimes are summarized in Table 1.

Metal-ion dopant	Number of events ( <i>N</i> )	Mean lifetime ( $\tau$ ) / $\mu\text{s}$
copper only	575	$39.9 \pm 0.8$
silver/copper	601	$12.7 \pm 0.7$

**Table 1.** Results of analysis of distributions of XTL lifetimes. See Figure 3 for the dopant-ion concentrations used and the corresponding histograms. The uncertainties represent 95% confidence intervals for the mean lifetime.



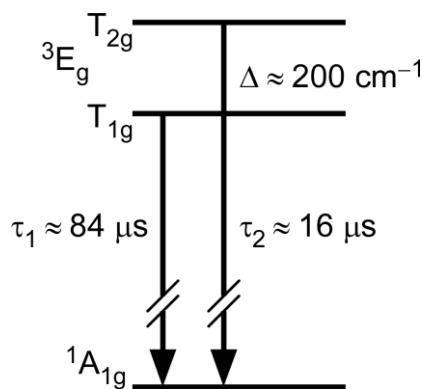
**Figure 3.** Histograms of the lifetimes for XTL of NaCl solutions. Dopant-ion concentrations (mole ratios) were 1900 ppm  $\text{Cu}^{2+}/\text{Na}^+$  and 530 ppm  $\text{Ag}^+/\text{Na}^+$ . For the results in blue (copper only), solutions were doped only with copper ions; for the results in yellow (silver/copper), solutions were doped with both copper and silver ions.



The lifetimes in Figure 3 range between 2.5 to 65  $\mu\text{s}$ , and are distinctly higher for solutions doped only with copper ions. With the addition of silver ions there is a peak at 9  $\mu\text{s}$ , and a tail in the distribution towards higher lifetimes. Based on the XTL emission spectrum, the emitting species were considered to be  $\text{Cu}^+$  and  $\text{Ag}^+$  substitutional defects in NaCl.<sup>24</sup> These assignments were based on previously published structure calculations and photoluminescence (PL) spectra.<sup>26-29</sup> The metal ions for these defects substitute directly for  $\text{Na}^+$  in the rock-salt crystal lattice. The crystal ionic radius of  $\text{Ag}^+$  (1.15 Å) and  $\text{Cu}^+$  (0.77 Å) are both similar to  $\text{Na}^+$  (1.02 Å).<sup>30</sup> For the silver dimer  $(\text{Ag}^+)_2$  species, Atoussi et al. conducted PL polarization measurements using ultraviolet excitation of single NaCl crystals intentionally doped with  $\text{Ag}^+$ . Their results showed that the two silver ions are separated by a single  $\text{Cl}^-$  anion and are oriented along the  $C_4$  axis of the crystal.<sup>31-32</sup>

#### 4. Discussion

UV photoluminescence emission lifetimes for NaCl doped with  $\text{Cu}^+$  and with  $\text{Ag}^+$  have been measured by Bosi et al.,<sup>33-34</sup> and the lifetime for the silver dimer  $(\text{Ag}^+)_2$  has been measured by Kurobori et al.<sup>35</sup> The PL lifetimes at room temperature (293 K) are summarized in Table 2. Although the assignment of the electronic states is not known, the short lifetime for  $(\text{Ag}^+)_2$  is consistent with decay from a singlet excited state.<sup>35</sup> The lifetimes for the single-ion species ( $\text{Ag}^+$  and  $\text{Cu}^+$ ) have been found to decrease with temperature, approaching an asymptotic value at higher temperatures ( $T \gg 300$  K). The temperature dependence has been interpreted in terms of the splitting ( $\Delta \sim 200 \text{ cm}^{-1}$ ) of the excited triplet state  $^3\text{E}_g$  into two components,  $\text{T}_{2g}(^3\text{E}_g)$  and  $\text{T}_{1g}(^3\text{E}_g)$ , as illustrated in Figure 4. The upper  $\text{T}_{2g}(^3\text{E}_g)$  triplet state gains some singlet character through mixing with a higher  $^1\text{T}_{2g}$  state, so that transition to the ground singlet state  $^1\text{A}_{1g}$  becomes partially spin-allowed.<sup>36</sup> For the lower  $\text{T}_{1g}(^3\text{E}_g)$  triplet state, however, the transition to the ground state is largely spin forbidden. The lifetime of the upper state ( $\sim 16 \mu\text{s}$ ) is therefore much shorter than the so-called ‘metastable’ lower state ( $\sim 84 \mu\text{s}$ ). Transitions take place from both states, and the lifetime observed depends on the temperature-dependent population of the two states. The work of Bosi et al. suggests that  $\Delta$  also changes with  $T$  as a result of the equilibrium position of the ion at the defect; however, the two-state model can still be applied over different ranges at low or high  $T$ .<sup>37</sup> The lifetimes at room temperature for these systems are close to the asymptotic (high temperature) limit.



**Figure 4.** Schematic energy-level diagram showing luminescence of  $\text{Cu}^+$  substitutional defect in the NaCl lattice. The luminescence consists of two components from the  $^3\text{E}_g$  electronic excited triplet states to the ground singlet state  $^1\text{A}_{1g}$ . The resulting lifetime is found to depend on temperature (see text for details). The lifetime values indicated were obtained by fitting the PL data of Bosi et al. in the range 97–300 K.<sup>33</sup>

The mean lifetime of  $39.9 \mu\text{s}$  measured for XTL of NaCl doped with copper ions (Table 1) is remarkably close to the PL lifetime of  $39.2 \mu\text{s}$  (Table 2), so we assign  $\text{Cu}^+$  as the emitting species.<sup>33</sup> The results tell us that a stable crystal has been formed very fast ( $< 10 \text{ ns}$ ) and can luminesce at the natural (equilibrium) rate. If the XTL and PL lifetimes were significantly different, or the decay was multi-exponential, it would suggest the transformation to crystal is a longer or more-complex process. As we have outlined in our previous report, the mechanism for production of the excited dopant ions can be understood in terms of transformation of the cluster over a set of multidimensional electronic potential energy surfaces.<sup>24</sup> As the cluster rearranges towards crystallinity, the dopant ions may become trapped in the triplet excited states and subsequently luminesce. The range of lifetimes observed can be explained assuming a distribution of final temperatures and therefore populations of the two excited triplet states.

It is remarkable that the XTL emission is assigned to  $\text{Cu}^+$ , whereas the aqueous dopant used was  $\text{Cu}^{2+}$ . In aqueous solution,  $\text{Cu}^+$  is liable to disproportionation into  $\text{Cu}^0$  and  $\text{Cu}^{2+}$ . It is therefore unlikely that  $\text{Cu}^+$  ions originated from the  $\text{CuSO}_4$  solution used, even though  $\text{Cu}^+$  can be stabilized in concentrated HCl due to formation of  $[\text{CuCl}_2]^-$ . A plausible explanation is that the reduction of  $\text{Cu}^{2+}$  occurs as a solute cluster collapses into the crystalline state. The ionization energy of  $\text{Cu}^+$  is  $1960 \text{ kJ mol}^{-1}$  and the electron affinity of  $\text{Cl}^-$  is  $349 \text{ kJ mol}^{-1}$ ,<sup>30</sup> so electron transfer is energetically favorable. The enthalpy of fusion for NaCl is  $28 \text{ kJ mol}^{-1}$ ,<sup>30</sup> and we calculate that the energy released for solidification of a cluster of 1 nm radius is equivalent to  $1900 \text{ kJ mol}^{-1}$ . In justification of this mechanism, we note that Patil and Moharil achieved  $\text{Cu}^+$  doping of rocksalt simply by mixing solid

NaCl and CuCl<sub>2</sub>, followed by melting and quenching to low temperature.<sup>38</sup> Moreover, Sellner et al. have argued that the strong electric fields in concentrated sodium chloride solutions may be responsible for electron transfer and redistribution during nucleation.<sup>4</sup> Although our calculation is based on the liquid-to-solid transition, it illustrates that a significant amount of energy may be available during formation of the crystal from the putative liquid-like cluster in solution.

<b>Metal-ion dopant</b>	<b>Photoluminescence lifetime (<math>\tau</math>) / <math>\mu</math>s</b>
copper Cu <sup>+</sup>	39.2
silver Ag <sup>+</sup>	27.6
silver dimer (Ag <sup>+</sup> ) <sub>2</sub>	0.0052

**Table 2.** UV photoluminescence lifetimes for copper (Cu<sup>+</sup>) and silver (Ag<sup>+</sup>) ions doped into crystalline NaCl. The values for single ions were obtained at  $T = 20$  °C, as interpolated from experimental values of Bosi et al.<sup>33-34</sup> The value for silver-ion dimer was taken from Kurobori et al.<sup>35</sup>

The mean lifetime of 12.7  $\mu$ s measured for XTL with silver and copper ions (Table 1) is shorter than the PL values for single-ion species, but longer than that of the dimer (Table 2). This suggests that energy transfer takes place between donor and acceptor species. We assume that on collapse of a cluster, all three of the luminescent species are excited instantaneously. These species will be present at varying concentrations in different clusters. We consider emission from the silver ions first, and then copper ions.

For silver ions, due to the short lifetime, the initially excited silver dimer species will luminesce relatively quickly (lifetime 5.2 ns) leaving a population of ground-state (Ag<sup>+</sup>)<sub>2</sub>. Likewise, the initially excited Ag<sup>+</sup> species would normally proceed to decay with a lifetime of 27.6  $\mu$ s. However, since the concentration of Ag<sup>+</sup> in the cluster is sufficiently high, it is possible that non-radiative resonant energy transfer takes place from excited Ag<sup>+</sup> to ground-state (Ag<sup>+</sup>)<sub>2</sub>, followed by emission from the excited dimer. This would reduce the observed lifetime compared to that of isolated Ag<sup>+</sup> ions. The <sup>3</sup>E<sub>g</sub> states of the Ag<sup>+</sup> center are ~5.0 eV (equivalent to 250 nm) above the ground state, which is close to the known absorption maximum of the silver dimer ~5.4 eV (230 nm).<sup>29, 35</sup> The acceptor electronic state for (Ag<sup>+</sup>)<sub>2</sub> is not known: the energy transfer mechanism could be either spin-allowed dipole–dipole (Förster mechanism) or spin-forbidden (Dexter mechanism).<sup>39</sup> The tail in the histogram of lifetimes for the mixed silver/copper system (Figure 3)

indicates events with longer lifetimes, which we ascribe to emissions from single-ion species ( $\text{Ag}^+$  or  $\text{Cu}^+$ ) in clusters with lower concentrations of dopants.

For copper ions, transfer from excited  $\text{Cu}^+$  to ground-state  $(\text{Ag}^+)_2$  is unlikely since the  $^3\text{E}_g$  states of  $\text{Cu}^+$  are much lower in energy  $\sim 3.4$  eV (equivalent to 360 nm). From the integrated intensities of the peaks in the XTL emission spectrum, the relative contributions of the species to the total emission are  $\text{Ag}^+$  (39%),  $\text{Cu}^+$  (10%) and  $(\text{Ag}^+)_2$  (51%).<sup>24</sup> The fraction of events with  $\tau > 25$   $\mu\text{s}$  is 10%, which is close in value to the relative contribution of  $\text{Cu}^+$  to the emission spectrum. So it may be that these longer-lifetime events are from clusters that contain predominantly  $\text{Cu}^+$  ions. We conclude, therefore, that the mean lifetime observed in XTL of NaCl doped with copper and silver ions is due predominantly to emission from  $\text{Ag}^+$  and  $(\text{Ag}^+)_2$  species, including non-resonant energy transfer from electronically excited  $\text{Ag}^+$  to ground-state  $(\text{Ag}^+)_2$ .

As noted in section 2, we have found that it is not possible to obtain good XTL by doping solutions only with silver ions. The reason for this is not clear. It may be that  $\text{Cu}^{2+}$  plays a role as a structure-making cation in solution.<sup>15</sup> Alternatively, it may be that the reduction of  $\text{Cu}^{2+}$ , outlined above, plays a key role in stimulating rapid nucleation to obtain XTL. This hypothesis could be evaluated by studying the XTL of known mixtures of  $\text{CuCl}_2$  and  $\text{CuCl}$  dopants dissolved directly into the concentrated HCl solution in order to protect the  $\text{Cu}^+(\text{aq})$  from disproportionation. Detailed time-resolved studies of NaCl solutions doped with lead ions, where the emission pulses are much shorter ( $< 80$  ns) may provide further information about the dynamics of nucleation at shorter times. Finally, we note that computational modelling of our proposed mechanism might be tackled on the basis of two distinct timescales. The desolvation and cluster re-organization over longer times may be modelled using molecular dynamics, whereas the luminescence from excited state species would require electronic structure calculations.<sup>4, 13-14</sup>

## 5. Conclusions

In summary, we have conducted measurements of the luminescence decay lifetime for XTL of sodium chloride solutions doped with trace amounts of copper and silver ions. No RF or acoustic signals were observed, and therefore TL of nascent crystals was ruled out as a cause of the XTL. Emissions were assigned to  $\text{Cu}^+$ ,  $\text{Ag}^+$  and  $(\text{Ag}^+)_2$  substituent-ion defect species in the NaCl crystal lattice. The distribution of lifetimes was found to lie in the range 2.5–65  $\mu\text{s}$ . The mean lifetime for XTL with solutions doped only with copper ions was found to be identical to the previously measured UV PL lifetime of solid NaCl doped with  $\text{Cu}^+$ . This observation, coupled with

the fast rise-time of the XTL emission events, suggests that all the substituent ions in a crystal are excited instantaneously (within 10 ns). The mean lifetime for XTL with copper and silver-ion dopants was found to lie between the values of the PL lifetime for the three emission species, which was attributed to resonant electronic energy transfer between electronically excited  $\text{Ag}^+$  and ground-state  $(\text{Ag}^+)_2$ . Our study demonstrates that dopant metal ions can act as valuable reporters of the electronic environment during nucleation of simple inorganic salts. Further theoretical studies on the effects of electric fields and the electron transfer within nascent salt crystals may shed further light on the dynamics of crystal nucleation.

## Acknowledgements

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